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(54) **HOSE MADE OF THERMOPLASTIC ELASTOMER**

(57) The hose of the invention comprises a thermoplastic elastomer having a softening temperature of 160°C or above as measured by a TMA softening temperature measuring apparatus, elongation at break of at least 200% as determined at a testing rate of 100 mm/min, initial flexural modulus of from 20 to 700 MPa as measured at a testing rate of 2 mm/min, and a volume change of -2 to +10% after 168 hours of soaking in a 50%-ethylene glycol aqueous solution at 100°C. In particular, the hose preferably comprises a thermoplastic elastomer comprising 15 to 95 parts by mass of an olefin

resin (A) that contains 50 to 97 % by mass of a specific 4-methyl-1-pentene polymer (A1) and 3 to 50 % by mass of an olefin resin (A2) other than the 4-methyl-1-pentene polymer (A1), and 5 to 85 parts by mass of a crosslinked rubber (B) (components (A) and (B) total 100 parts by weight).

The hose comprising the thermoplastic elastomer of the invention can be readily molded and recycled, is excellent in heat resistance, water resistance and mechanical characteristic, and has a low specific gravity.

Description**FIELD OF THE INVENTION**

- 5 [0001] The present invention relates to a hose comprising a thermoplastic elastomer, more particularly to a vulcanized rubber hose suitable as an automotive water hose of excellent heat resistance.

BACKGROUND ART

- 10 [0002] Vulcanized rubber hoses have good flexibility and heat resistance, and are widely used as various automotive hoses and industrial hot-water hoses and steam hoses.

- [0003] Production of the vulcanized rubber hoses, however, necessarily comprises multiple steps of kneading various compounding chemicals, extrusion, braiding and vulcanization, and therefore requires a long time. Moreover, waste materials by the molding and used molded products are difficult to recycle, causing waste problems. The vulcanized rubberhose, when used as an automotive water hose, can cause other problems such as electrical corrosion resulting from carbon black used as a reinforcing agent, formation of a salt by zinc oxide compounded, and hindrance to valve action by the salt formation. Also, recent movements for fuel saving and environmental friendliness in the automobile industry have created trends of lightweight automotive parts.

- 20 [0004] To deal with the above problems, thermoplastic elastomers have been studied for use in place of the vulcanized rubbers, but no thermoplastic elastomers have been obtained that are readily moldable and recyclable, excellent in heat resistance, water resistance and mechanical characteristics, and can provide hoses having low specific gravities.

- [0005] Accordingly the advent of thermoplastic elastomers capable of providing hoses that are readily moldable and recyclable and are excellent in heat resistance, water resistance and mechanical characteristics, and hoses of the thermoplastic elastomers has been expected.

- 25 [0006] The present invention has an object of providing a thermoplastic elastomer hose that is readily moldable and recyclable, excellent in heat resistance, water resistance and mechanical characteristics, and has a low specific gravity.

SUMMARY OF THE INVENTION

- 30 [0007] The hose according to the present invention comprises a thermoplastic elastomer having a softening temperature of 160°C or above as measured by a TMA softening temperature measuring apparatus, elongation at break of at least 200% as determined at a testing rate of 100 mm/min, initial flexural modulus of from 20 to 700 MPa as measured at a testing rate of 2 mm/min, and a volume change of -2 to +10% after 168 hours of soaking in a 50%-ethylene glycol aqueous solution at 100°C.

- 35 [0008] The thermoplastic elastomer hose preferably comprises an olefin thermoplastic elastomer. Specifically, the hose is preferably obtained by molding an olefin thermoplastic elastomer comprising:

15 to 95 parts by mass of an olefin resin (A), and

40 5 to 85 parts by mass of a crosslinked rubber (B), wherein the components (A) and (B) total 100 parts by mass.

- [0009] More preferably, the thermoplastic elastomer hose comprises the olefin thermoplastic elastomer in which 50 to 97 % by mass of the olefin resin (A) is a 4-methyl-1-pentene polymer (A1),

- 45 the polymer (A1) being a 4-methyl-1-pentene homopolymer and/or a 4-methyl-1-pentene/ α -olefin random copolymer containing 80 to 99.9 % by mass of 4-methyl-1-pentene and 0.1 to 20 % by mass of an α -olefin of 2 to 20 carbon atoms.

- [0010] Preferably, an olefin resin (A2) other than the 4-methyl-1-pentene polymer (A1) in the olefin resin (A) is a peroxide-decomposable, olefin resin.

- 50 [0011] Preferably, the crosslinked rubber (B) is a crosslinked product of a peroxide-crosslinkable olefin copolymer rubber.

- [0012] The hose comprising the thermoplastic elastomer of the invention is suitable as an automotive water hose.

BEST MODE TO CARRY OUT THE INVENTION

- 55 [0013] The hose comprising the thermoplastic elastomer of the invention will be described in detail, hereinafter.

- [0014] The thermoplastic elastomer hose is preferably obtained by molding the olefin thermoplastic elastomer containing:

the olefin resin (A), preferably the 4-methyl-1-pentene polymer (A1) and the olefin resin (A2) other than the 4-methyl-1-pentene polymer (A1) and the crosslinked rubber (B).

5 [0015] These components of the thermoplastic elastomer are described first.

Olefin Resin (A)

10 [0016] The olefin resin (A) for use in the invention preferably contains the 4-methyl-1-pentene polymer (A1) in 50 to 97 % by mass and the olefin resin (A2) other than the 4-methyl-1-pentene polymer (A1) in 3 to 50 % by mass.

[4-Methyl-1-Pentene Polymer (A1)]

15 [0017] The 4-methyl-1-pentene polymer (A1) is a 4-methyl-1-pentene homopolymer or a 4-methyl-1-pentene/ α -olefin random copolymer containing 80 to 99.9 % by mass, preferably 90 to 99.9 % by mass of 4-methyl-1-pentene and 0.1 to 20 % by mass, preferably 0.1 to 10 % by mass of an α -olefin of 2 to 20, preferably 6 to 20 carbon atoms.

20 [0018] In the case of the 4-methyl-1-pentene/ α -olefin random copolymer, the α -olefin copolymerized with 4-methyl-1-pentene is, for example, an α -olefin of 2 to 20, preferably 6 to 20 carbon atoms, such as ethylene, propylene, 1-butene, 1-hexene, 1-octene, 1-decene, 1-dodecene, 1-tetradecene, 1-hexadecene, 1-octadecene or 1-eicosene. These α -olefins may be used singly or in combination of two or more kinds for copolymerization with 4-methyl-1-pentene.

25 [0019] When the 4-methyl-1-pentene polymer (A1) is a copolymer, the copolymer preferably comprises 4-methyl-1-pentene as a main component in a content of 80 to 99.9 % by mass, preferably 90 to 99.9 % by mass, and a copolymerization component in a content of 0.1 to 20 % by mass, preferably 0.1 to 10 % by mass. When the content of the copolymerization component is in the above range, the resulting thermoplastic elastomer can have more superior heat resistance.

[0020] The 4-methyl-1-pentene polymer (A1) ideally has a melt flow rate (MFR: ASTM D1238, 260°C, 5.0 kg load) of 0.1 to 200 g/10 min, preferably 1 to 150 g/10 min.

30 [0021] The 4-methyl-1-pentene polymer (A1) may be a commercially available product, such as Mitsui Chemicals Inc. products: TPXMX001, MX002, MX004, MX021, MX321, RT18 and DX845 (trademark). Other companies' 4-methyl-1-pentene polymers are also preferable to use if they meet the above conditions.

[0022] The 4-methyl-1-pentene polymer (A1) may be used individually or in combination of two or more kinds.

[0023] The 4-methyl-1-pentene polymer (A1) plays a role to improve in particular the heat resistance of the thermoplastic elastomer hose of the invention.

35 [Olefin Resin (A2)]

[0024] The olefin resin (A2) for use in the invention is an olefin resin other than the 4-methyl-1-pentene polymer (A1), and comprises a high-molecular-weight solid product obtained by homopolymerization or copolymerization of at least one monoolefin by either a high-pressure process or a low-pressure process.

40 [0025] Examples of the olefin resin (A2) include isotactic or syndiotactic monoolefin homopolymer or copolymer resins. These representative resins are commercially available.

45 [0026] Examples of suitable raw olefins for the olefin resin (A2) include α -olefins of 2 to 12, preferably 2 to 10 carbon atoms, such as ethylene, propylene, 1-butene, 1-pentene, 1-hexene, 1-octene, 1-decene, 2-methyl-1-propene, 3-methyl-1-pentene, 4-methyl-1-pentene and 5-methyl-1-hexene. These olefins may be used either individually or as a mixture of 2 or more kinds.

[0027] The polymerization may be carried out by any mode, randomly or blockwise, as long as it can produce resin-like products.

[0028] The olefin resin (A2) may be used singly or in combination of two or more kinds.

[0029] A peroxide-decomposable olefin resin is preferable as the olefin resin (A2).

50 [0030] Particularly preferably, the peroxide-decomposable olefin resin is a propylene polymer, such as a propylene homopolymer, a propylene/ethylene block copolymer, a propylene/ethylene random copolymer or a propylene/ethylene/butene random copolymer.

[0031] The olefin resin (A2) for use in the invention ideally has a melt flow rate (MFR: ASTM D1238-65T, 230°C) of 0.01 to 1000 g/10 min, preferably 0.05 to 500 g/10 min.

55 [0032] The olefin resin (A2) plays a role to improve dispersion of the crosslinked rubber (B) and the 4-methyl-1-pentene polymer (A1) and to enhance flowability and mechanical strength of the thermoplastic elastomer used in the invention.

Crosslinked Rubber (B)

[0033] The crosslinked rubber (B) for use in the invention can be a crosslinked rubber of known crosslinkable raw rubber and is not limited. Preferably, the crosslinked rubber (B) is a crosslinked product of a peroxide-crosslinkable olefin copolymer rubber whose raw rubber is preferably a conventional ethylene/ α -olefin/non-conjugated polyene copolymer rubber or ethylene/ α -olefin copolymer rubber.

[0034] The raw rubber is preferably an ethylene/ α -olefin/non-conjugated polyene copolymer rubber, and is particularly preferably an ethylene/propylene/non-conjugated diene rubber having the following properties.

[0035] The ethylene/propylene/non-conjugated diene rubber has a molar ratio of contents of structural units derived from ethylene to contents of structural units derived from propylene [ethylene/propylene (molar ratio)] of 30/70 to 90/10, preferably 50/50 to 85/15, an iodine value of 1 to 40 g/100 g, preferably 3 to 30 g/100 g, and an intrinsic viscosity $[\eta]$ determined at 135°C in decalin (decahydronaphthalene) of 0.8 to 6 dl/g, preferably 1 to 5 dl/g.

[0036] Examples of the non-conjugated polyene include chain non-conjugated dienes, such as 1,4-hexadiene, 3-methyl-1,4-hexadiene, 4-methyl-1,4-hexadiene, 5-methyl-1,4-hexadiene, 4,5-dimethyl-1,4-hexadiene and 7-methyl-1,6-octadiene;

cyclic non-conjugated dienes, such as methyltetrahydroindene, 5-ethylidene-2-norbornene, 5-methylene-2-norbornene, 5-isopropylidene-2-norbornene, 5-vinylidene-2-norbornene, 6-chloromethyl-5-isopropenyl-2-norbornene and dicyclopentadiene; and

trienes, such as 2, 3-diisopropylidene-5-norbornene, 2-ethylidene-3-isopropylidene-5-norbornene and 2-propenyl-2,2-norbornadiene. Of these, preferable are 5-ethylidene-2-norbornene, 5-vinylidene-2-norbornene and dicyclopentadiene. The non-conjugated polyenes may be used either individually or in combination of two or more kinds.

[0037] The crosslinked rubber (B) may be used singly or in combination of two or more kinds.

Other Components

[0038] Known additives, such as softeners, inorganic fillers and carbon blacks, may be according to necessity compounded in the thermoplastic elastomer in addition to the olefin resin (A) [the 4-methyl-1-pentene polymer (A1) and the olefin resin (A2) other than the 4-methyl-1-pentene polymer (A1)] and the crosslinked rubber (B) within limits not detrimental to the object of the present invention.

[0039] The softeners employable in the invention are those commonly used in rubbers.

[0040] Specific examples of the softeners include:

petroleum substances, such as process oils, lubricating oils, paraffins, fluid paraffins, petroleum asphalts and vaselines;

coal tars, such as coal tars and coal tar pitches;

fatty oils, such as castor oil, linseed oil, colza oil, soybean oil and coconut oil;

waxes, such as tall oils, beeswaxes, carnauba waxes and lanolins;

fatty acids, such as ricinoleic acid, palmitic acid, stearic acid, barium stearate and calcium stearate, and metal salts of these acids;

synthetic polymer materials, such as petroleum resins, coumarone-indene resins and atactic polypropylenes;

ester plasticizers, such as dioctyl phthalate, dioctyl adipate and dioctyl sebacate;

microcrystalline waxes, rubber substitutes (factices), synthetic olefin oils, liquid polybutadienes, modified liquid polybutadienes and liquid Thiokol.

[0041] In the invention, the softener is ideally used in a proportion of 100 parts by mass or less, preferably 80 parts by mass or less, more preferably 60 parts by mass or less based on 100 parts by mass in total of the 4-methyl-1-pentene polymer (A1), the olefin resin (A2) and the crosslinked rubber (B). When the softener is used in the above proportion, the resulting thermoplastic elastomer can exhibit an excellent flowability in the molding and the hose obtained therefrom does not suffer lowering in mechanical properties.

[0042] In the invention, the softener may be added at the time of production of the thermoplastic elastomer or may have been mixed with the raw rubber for oil extension.

[0043] Examples of the inorganic fillers for use in the invention include calcium carbonate, calcium silicate, clays, kaolins, talcs, silicas, diatomaceous earths, powdered mica, asbestos, aluminas, barium sulfate, aluminum sulfate, calcium sulfate, basic magnesium carbonate, molybdenum disulfide, graphites, glass fibers, glass beads, Shirasu balloons, basic magnesium sulfide whiskers, calcium titanate whiskers and aluminum borate whiskers.

[0044] In the invention, the inorganic filler is ideally used in a proportion of 100 parts by mass or less, preferably 80 parts by mass or less based on 100 parts by mass in total of the 4-methyl-1-pentene polymer (A1), the olefin resin (A2) and the crosslinked rubber (B).

[0045] When the inorganic filler is used in the above proportion, the resulting thermoplastic elastomer can have excellent rubber elasticity and moldability and workability.

[0046] In the invention, conventional additives, such as heat stabilizers, anti-aging agents, weathering stabilizers, antistatic agents and lubricants (e.g., metallic soaps and waxes), may be added, to the thermoplastic elastomer within limits not detrimental to the object of the invention.

Thermoplastic Elastomer

[0047] The thermoplastic elastomer used in the invention contains the olefin resin (A), preferably the 4-methyl-1-pentenepolymer (A1) and the olefin resin (A2) other than the 4-methyl-1-pentene polymer (A1), the crosslinked rubber (B) and the optional additives, such as the softeners, the inorganic fillers and the carbon blacks.

[0048] The thermoplastic elastomer ideally contains the crosslinked rubber (B) in a proportion of 5 to 85 parts by mass, preferably 10 to 85 parts by mass, and the olefin resin (A) in a proportion of 15 to 95 parts by mass in total, preferably 15 to 90 parts by mass in total, both based on 100 parts by mass in total of the olefin resin (A) and the crosslinked rubber (B).

[0049] More preferably, the thermoplastic elastomer contains the crosslinked rubber (B) in a proportion of 5 to 85 parts by mass, preferably 10 to 85 parts by mass, and the 4-methyl-1-pentene polymer (A1) and the olefin resin (A2) other than the 4-methyl-1-pentene polymer (A1) in a proportion of 15 to 95 parts by mass in total, preferably 15 to 90 parts by mass in total, both based on 100 parts by mass in total of the 4-methyl-1-pentene polymer (A1), the olefin resin (A2) other than the 4-methyl-1-pentene polymer (A1) and the crosslinked rubber (B).

[0050] The 4-methyl-1-pentene polymer (A1) is contained in a proportion of 50 to 97 % by mass, preferably 55 to 95 % by mass, and the olefin resin (A2) other than the 4-methyl-1-pentene polymer (A1) is contained in a proportion of 3 to 50 % by mass, preferably 5 to 45 % by mass based on 100 % by mass in total of the 4-methyl-1-pentene polymer (A1) and the olefin resin (A2).

[0051] When the olefin resin (A) is contained in the above proportion, the resulting thermoplastic elastomer for hose can be excellent not only in mechanical characteristics but also in moldability and workability. The hose of the invention can be obtained from the thermoplastic elastomer.

[0052] When the crosslinked rubber (B) is contained in the above proportion, the resulting thermoplastic elastomer for hose can have superior flexibility, permanent set resistance and flexural fatigue resistance.

[0053] When the olefin resin (A) contains the 4-methyl-1-pentene polymer (A1) in the above proportion, the resulting thermoplastic elastomer for hose can be excellent in flexural modulus and heat resistance.

[0054] The thermoplastic elastomer of the invention is readily recyclable because, in addition to the inherent easy recyclability of the thermoplastic elastomers, it is prepared from an olefin raw material.

[0055] The thermoplastic elastomer may be obtained by mixing together the 4-methyl-1-pentene polymer (A1), the olefin resin (A2), a raw rubber for the crosslinked rubber (B) and the optional additives, such as the softeners and the inorganic fillers, and dynamically heat treating the mixture in the presence of a crosslinking agent.

[0056] The term "dynamically heat treating" used herein means that the mixture is kneaded in a molten state.

[0057] The thermoplastic elastomer for use in the invention can be obtained also by dynamically heat treating a mixture of the olefin resin (A2) and a raw rubber for the crosslinked rubber (B) in the presence of a crosslinking agent, thereby preparing a masterbatch, and dynamically heat treating the masterbatch and the 4-methyl-1-pentene polymer (A1). According to necessity, the additives, such as the softeners and the inorganic fillers, may be compounded with the masterbatch or added in the mixing of the masterbatch and the 4-methyl-1-pentene polymer (A1).

[0058] Examples of the crosslinking agent include those commonly used for thermosetting rubbers, such as organic peroxides, phenolic resins, sulfur, hydrosilicone compounds, amino resins, quinones, quinone derivatives, amine compounds, azo compounds, epoxy compounds and isocyanates. Of these crosslinking agents, organic peroxides are particularly preferable.

[0059] Examples of the organic peroxides employable in the invention include dicumyl peroxide, di-tert-butyl peroxide, 2,5-dimethyl-2,5-di-(tert-butylperoxy)hexane, 2,5-dimethyl-2,5-di-(tert-butylperoxy)hexyne-3, 1,3-bis(tert-butylperoxyisopropyl)benzene, 1,1-bis(tert-butylperoxy)-3,3,5-trimethylcyclohexane, n-butyl-4,4-bis(tert-butylperoxy)valerate, benzoyl peroxide, p-chlorobenzoyl peroxide, 2,4-dichlorobenzoyl peroxide, tert-butylperoxy benzoate, tert-butylperbenzoate, tert-butylperoxyisopropyl carbonate, diacetyl peroxide, lauroyl peroxide and tert-butylcumyl peroxide.

[0060] Of these, in view of odor and scorch stability, preferable are 2,5-dimethyl-2,5-di-(tert-butylperoxy)hexane, 2,5-dimethyl-2,5-di-(tert-butylperoxy)hexyne-3 and 1,3-bis(tert-butylperoxyisopropyl)benzene, and most preferred is 2,5-dimethyl-2,5-di-(tert-butylperoxy)hexane.

[0061] The organic peroxide is ideally used in an amount of 0.02 to 5 parts by mass, preferably 0.05 to 3 parts by mass based on 100 parts by mass in total of the materials to be treated: the 4-methyl-1-pentene polymer (A1), the olefin resin (A2) and a raw rubber for the crosslinked rubber (B). When the organic peroxide is used in the above proportion, the resulting thermoplastic elastomer for hose can be excellent in heat resistance, tensile properties, elastic

recovery and impact resilience, mechanical strength and elongation.

[0062] In the invention, the crosslinking treatment with the organic peroxide may be accompanied by addition of a peroxy crosslinking auxiliary, such as sulfur, p-quinone dioxime, p,p'-dibenzoyl quinone dioxime, N-methyl-N-4-dinitrosoaniline, nitrosobenzene, diphenylguanidine or trimethylolpropane-N,N'-m-phenylene dimaleimide; or a polyfunctional methacrylate monomer, such as divinylbenzene, triallyl cyanurate, triallyl isocyanurate, ethylene glycol dimethacrylate, diethylene glycol dimethacrylate, polyethylene glycol dimethacrylate, trimethylolpropane trimethacrylate or allyl methacrylate; or a polyfunctional vinyl monomer, such as vinyl butyrate or vinyl acetate.

[0063] With the above compound used, uniform and proper crosslinking can be expected. In the invention, the polyfunctional methacrylate monomer is preferable, and particularly divinyl benzene, triallyl cyanurate and triallyl isocyanurate are preferable.

[0064] The polyfunctional methacrylate monomer is easy to handle, has good compatibility with the materials to be crosslinked: the main component, 4-methyl-1-pentene polymer (A1), the olefin resin (A2) and a raw rubber for the crosslinked rubber (B), and has a function of solubilizing the organic peroxide to work as a dispersant for the organic peroxide so that the crosslinking by heat treatment can be effected uniformly to give a thermoplastic elastomer well balanced in flowability and physical properties.

[0065] The crosslinking auxiliary or the compound, such as the polyfunctional vinyl monomer, is ideally used in an amount of 5 parts by mass or less, preferably 0.1 to 3 parts by mass based on 100 parts by mass in total of the materials to be treated.

[0066] A decomposition accelerator may be used to promote decomposition of the organic peroxide, and examples thereof include tertiary amines, such as triethylamine, tributylamine and 2,4,6-tri(dimethylamino)phenol, and naphthenates of aluminum, cobalt, vanadium, copper, calcium, zirconium, manganese, magnesium, zinc and mercury.

[0067] The dynamic heat treatment is preferably carried out in a closed apparatus, and further preferably in an atmosphere of an inert gas, such as nitrogen or carbon dioxide.

[0068] The heat treatment temperature ranges from the melting point of the olefin resin (A) [the 4-methyl-1-pentene polymer (A1) and the olefin resin (A2)] to 300°C, and usually in the range of 150 to 280°C, preferably 170 to 260°C. The kneading time is from 1 to 20 minutes, preferably 1 to 10 minutes. The shear force applied is from 10 to 50,000 sec⁻¹, preferably 100 to 20,000 sec⁻¹ in shear rate.

[0069] The kneading apparatus for use in the invention, which is preferably a closed type, can be a mixing mill, an intensive mixer (e.g., a Banbury mixer or a kneader), or a single- or twin-screw extruder, and is particularly preferably a twin-screw extruder.

[0070] According to the present invention, the thermoplastic elastomer comprising the 4-methyl-1-pentene polymer (A1), the olefin resin (A2) and the crosslinked rubber (B) can be obtained by the aforesaid dynamic heat treatment.

[0071] In the invention, that the rubbers in the thermoplastic elastomer are crosslinked means that when the thermoplastic elastomer is soaked in cyclohexane at 23°C for 48 hours for extraction, the ratio of the remaining rubbers amount to the mixed rubbers amount on percentage, which is otherwise understood as the percentage of the gel amount, is preferably 30 % by mass or more, more preferably 50 % by mass or more.

[0072] In the mixing of the 4-methyl-1-pentene polymer (A1), the olefin resin (A2) and the crosslinked rubber (B), the aforesaid additives, such as the softeners, the inorganic fillers, the carbon blacks, the heat stabilizers, the anti-aging agents, the weathering stabilizers, the antistatic agents and the lubricants (e.g., metallic soaps and waxes), may be added. The additives are preferably mixed together with the components (A1), (A2) and (B) by the dynamic heat treatment, which is carried out at a temperature not lower than the melting point of the 4-methyl-1-pentene polymer (A1). Specifically the heat treatment temperature is in the range of 240 to 300°C, preferably 240 to 270°C.

[0073] The thermoplastic elastomer of the invention ideally has a softening temperature of 160°C or above, preferably 170°C or above, more preferably 180°C or above.

[0074] The upper limit of the softening temperature in view of moldability and the like should be preferably 240°C, more preferably 230°C. The softening temperature is determined with a TMA softening temperature measuring apparatus by measuring a temperature at which penetration of a 49 g-loaded needle into a sample being heated at a rate of 20°C/min reaches 0.1 mm.

[0075] The thermoplastic elastomer for use in the invention has an elongation at break, as measured by a method defined in JIS K 6251 (testing rate: 100 mm/min), of at least 200%, preferably at least 250%. The greater elongation at break is the more preferable.

[0076] The thermoplastic elastomer for use in the invention desirably has initial flexural modulus of from 20 to 700 MPa, preferably from 20 to 600 MPa, more preferably from 30 to 500 MPa. The initial flexural modulus is a value determined by a method defined in JIS K 7171 (testing rate: 2 mm/min).

[0077] The thermoplastic elastomer used in the invention is desirably capable of forming a hose having a volume change of -2 to +10%, preferably 0 to +10% after 168 hours of soaking in a 50%-ethylene glycol aqueous solution at 100°C.

[0078] The thermoplastic elastomer for use in the invention ideally has a specific gravity of 0.83 to 0.89, preferably

0.83 to 0.88.

[0079] The thermoplastic elastomer, which is used in the invention as a raw material for various hoses, particularly for automotive water hoses, can also be used as a raw material for other products, such as automotive rack and pinion boots, constant velocity joint boots, dust covers, brake fluid reservoirs, washer tanks, temperature controls and air cleaner cases.

Hose

[0080] The hose according to the present invention is obtained by molding the thermoplastic elastomer.

[0081] The hose is readily moldable and recyclable, is excellent in heat resistance, water resistance and mechanical characteristics, and has a low specific gravity. The hose has exceptional heat resistance.

[0082] The hose, which is preferably used as an automotive water hose, has other utility as a reservoir hose, a ventilation hose, a vacuum hose, an air-injection hose, an air-cleaner hose, an industrial steam hose and an industrial hot-water hose.

[0083] The hose of the invention can be produced by a conventional molding method, such as extrusion molding, injection molding, extrusion blow molding or injection blow molding.

EFFECT OF THE INVENTION

[0084] The thermoplastic elastomer of the invention which preferably contains specific amounts of the olefin resin (A) [the 4-methyl-1-pentene polymer (A1) and the olefin resin (A2) other than the 4-methyl-1-pentene polymer (A1)] and the crosslinked rubber (B), is readily moldable and recyclable, has excellent heat resistance, water resistance and mechanical characteristics, and has a low specific gravity.

[0085] The thermoplastic elastomer hose of the invention comprises the aforesaid thermoplastic elastomer and therefore can be readily molded and recycled, has excellent heat resistance, water resistance and mechanical characteristics, and has a low specific gravity.

EXAMPLES

[0086] The present invention will be illustrated by the following Examples, which in no way limit the scopes of the invention.

[0087] The physical properties of olefin thermoplastic elastomers obtained in Examples and Comparative Examples were measured by the following methods.

[Methods for measuring physical properties]

(1) Tensile strength

[0088] In accordance with the method of JIS K 6251, a dumbbell type test piece No. 7 was subjected to a tensile test at a rate of 100 mm/min to measure the stress under which the test piece was broken.

(2) Elongation at break

[0089] In accordance with the method defined in JIS K 6251, a dumbbell type test piece No. 7 was stretched at a rate of 100 mm/min in a measuring environment of 23°C, and the nominal strain at break was measured.

(3) Initial flexural modulus

[0090] In accordance with the method defined in JIS K 7171, a 4-mm thick sheet was supported with a distance between the supports in a measuring environment of 23°C, and a load was applied to the center at a rate of 2 mm/min to determine the flexural modulus.

(4) Softening temperature

[0091] The softening temperature was determined with a TMA softening temperature measuring apparatus (produced by Du Pont K. K.) by measuring a temperature at which penetration of a 49 g-loaded needle into the thermoplastic elastomer being heated at a rate of 20°C/min reached 0.1 mm.

(5) Coolant resistance

[0092] In accordance with the method defined in JIS D 2602, the thermoplastic elastomer was soaked in a 50%-ethylene glycol aqueous solution at $100^{\circ}\text{C} \pm 1^{\circ}\text{C}$ for 168 hours, and changes in volume, elongation strength and elongation were measured.

Example 1

[0093] By means of a Henschel mixer were sufficiently mixed together:

25 parts by mass of pellets of a polypropylene homopolymer [MFR = 10 g/10 min (230°C , 2.16 kg load),
140 parts by mass of pellets of an oil-extended ethylene/propylene/5-ethylidene-2-norbornene (ENB) copolymer rubber [molar ratio of ethylene-derived units and propylene-derived units (ethylene/propylene) = 79/21, iodine value based on the ENB = 13, Mooney viscosity ML (1+4) at 125°C = 105, oil extension amount: 40 parts by mass of a mineral oil softener (PW-380TM produced by IDEMITSU KOSAN CO., LTD.) per 100 parts by mass of the rubber],
35 parts by mass of a post-addition mineral oil softener (aforesaid PW-380),
0.2 part by mass of an organic peroxide [2,5-dimethyl-2,5-di-(tert-butylperoxy)hexane],
0.2 part by mass of divinylbenzene (DVB), and
0.1 part by mass of a phenolic anti-aging agent. The mixture was fed to a twin-screw extruder and dynamically heat treated under the following conditions, thereby preparing masterbatch pellets of thermoplastic elastomer.

(Dynamic heat treatment conditions)

[0094]

■Extruder: ZSK-53TM produced by WERNER & PFLEIDERER, screw diameter = 53 mm.
■Temperature setting: C1/C2/C3/C4/C5/D = 140/160/180/220/220/200 ($^{\circ}\text{C}$).
■Maximum shear rate: 2800 (1/sec).
■Throughput: 50 (kg/h).

[0095] The thermoplastic elastomer masterbatch pellets, 50 parts by mass, were subsequently mixed together with 50 parts by mass of pellets of a 4-methyl-1-pentene polymer [TPX MX 002TM produced by Mitsui Chemicals, Inc.: 4-methyl-1-pentene content = 93 % by mass, content of mixed olefins of 16 carbon atoms and of 18 carbon atoms = 7 % by mass, MFR = 23 g/10 min (260°C , 5.0 kg load)] by a Henschel mixer. The mixture was fed to a twin-screw extruder and dynamically heat treated under the following conditions, thereby preparing pellets of thermoplastic elastomer for hose.

(Dynamic heat treatment conditions)

[0096]

■Extruder: ZSK-53TM produced by WERNER & PFLEIDERER, screw diameter = 53 mm.
■Temperature setting: C1/C2/C3/C4/C5/D = 200/240/260/270/270/250 ($^{\circ}\text{C}$).
■Maximum shear rate: 2000 (1/sec).
■Throughput: 60 (kg/h).

[0097] The above-obtained thermoplastic elastomer for hose contained the crosslinked rubber (B) in an amount of 31 % by mass, and the 4-methyl-1-pentene polymer (A1) and the olefin resin (A2) other than the 4-methyl-1-pentene polymer (A1) in a total amount of 69 % by mass based on 100 % by mass in total of the 4-methyl-1-pentene polymer (A1), the olefin resin (A2) and the crosslinked rubber (B). Based on the total 100 % by mass of the 4-methyl-1-pentene polymer (A1) and the olefin resin (A2), the contents of the 4-methyl-1-pentene polymer (A1) and of the olefin resin (A2) were 89 % by mass and 11 % by mass, respectively.

[0098] The pellets of thermoplastic elastomer for hose were injection molded into a given test piece, which was then subjected to measurement of tensile strength, elongation at break, initial flexural modulus and softening temperature by the above methods. Also, the thermoplastic elastomer was molded with a 45-mm \varnothing extruder at 280°C into a hose having an inner diameter of 20 mm and a radial thickness of 2 mm, from which a specified test piece was punched out and subjected to measurement of coolant resistances (changes in volume, tensile strength and elongation) by the

above measuring method.

[0099] The results are shown in Table 1.

Example 2

[0100] A thermoplastic elastomer for hose having a composition shown in Table 1 was obtained in the same manner as in Example 1, except that the components were added in different amounts.

[0101] The results of the measurements are shown in Table 1.

Example 3

[0102] A thermoplastic elastomer for hose having a composition shown in Table 1 was obtained in the same manner as in Example 1, except that the components were added in different amounts.

[0103] The results of the measurements are shown in Table 1.

Example 4

[0104] A thermoplastic elastomer for hose having a composition shown in Table 1 was obtained in the same manner as in Example 1, except that the components were added in different amounts.

[0105] The results of the measurements are shown in Table 1.

Example 5

[0106] This Example was carried out in the same manner as in Example 1, except that a 4-methyl-1-pentene copolymer [TPX RT 18™ produced by Mitsui Chemicals, Inc.: 4-methyl-1-pentene content = 97 % by mass, C₁₀ olefin content: 3 % by mass, MFR: 26 g/10 min (260°C, 5.0 kg load)] was used as the 4-methyl-1-pentene polymer (A1).

[0107] The results of the measurements are shown in Table 1.

Comparative Example 1

[0108] This Comparative Example was carried out in the same manner as in Example 1, except that use was made of thermoplastic elastomer pellets containing 95 parts by mass of the polypropylene homopolymer and 140 parts by mass of the oil-extended ethylene/propylene/5-ethylidene-2-norbornene copolymer rubber used in Example 1 but containing no TPX MX 002™ of Example 1.

[0109] The results of the measurements are shown in Table 2.

Comparative Example 2

[0110] This Comparative Example was carried out in the same manner as in Example 1, except that TPX MX 002™ alone was used as the 4-methyl-1-pentene polymer (A1).

[0111] The results of the measurements are shown in Table 2.

Comparative Example 3

[0112] This Comparative Example was carried out in the same manner as in Example 1, except that a commercially available polyolefin thermoplastic elastomer TPO (MILASTOMER 8030N™ produced by Mitsui Chemicals, Inc.) alone was injection molded and extrusion molded at 240°C.

[0113] The results of the measurements are shown in Table 2.

Comparative Example 4

[0114] This Comparative Example was carried out in the same manner as in Example 1, except that a commercially available polyamide thermoplastic elastomer TPAE (PEBAX 3533™ produced by Toray Industries Inc.) alone was injection molded and extrusion molded at 220°C.

[0115] The results of the measurements are shown in Table 2.

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Comparative Example 5

[0116] This Comparative Example was carried out in the same manner as in Example 1, except that a commercially available polyester thermoplastic elastomer TPEE (PELPRENE P30B™ produced by Toyobo Co., Ltd.) alone was injection molded and extrusion molded at 230°C.

[0117] The results of the measurements are shown in Table 2.

Table 1

		Example				
		1	2	3	4	5
Master batch *1	parts by mass	50	75	85	25	50
TPX MX 002	parts by mass	50	25	15	75	
TPX RT 18	parts by mass					50
(A1)+(A2) content *2	% by mass	69	47	37	86	69
Crosslinked rubber content *2	% by mass	31	53	63	14	31
(A2) content *3	% by mass	11	26	40	4	11
TPX MX 002 *3	% by mass	89	74	60	96	89
Tensile strength	MPa	9.5	8.0	7.6	11.7	10.7
Elongation at break	%	320	330	360	260	200
Initial flexural modulus	MPa	186	69	32	340	274
Softening temperature	°C	197	165	162	218	199
Coolant resistances *4						
Volume change	%	0.3	0.1	0.1	0.6	0.2
Tensile strength change	%	-4	-4	-2	-4	-7
Elongation change	%	-8	-9	-6	-13	-10
Specific gravity	-	0.85	0.86	0.86	0.84	0.85

*1: Master batch compounding

Oil-extended EPDM 140 parts by mass, mineral oil 34 parts by mass, polypropylene homopolymer 24 parts by mass, [2,5-dimethyl-2,5-di-(tert-butoxy)hexane] 0.2 part by mass, divinylbenzene (DVB) 0.2 part by mass and phenolic heat aging inhibitor 0.1 part by mass.

*2: Content based on 100 % by mass of a total of components (A1), (A2) and (B).

*3: Content based on 100 % by mass of a total of components (A1) and (A2).

*4: After soaking in distilled water/ethylene glycol = 50/50 (v/v) at 100°C for 168 hours.

Table 2

		Comparative Example				
		1	2	3	4	5
(A1)+(A2) content *1	% by mass	49	0			
Crosslinked rubber content *1	% by mass	51	0			
(A2) content *2	% by mass	100	0			
TPX MX 002 *2	% by mass	0	100			
MILASTOMER 8030N	Parts by mass			100		
PEBAX 3533	Parts by mass				100	
PELPRENE P30B	Parts by mass					100
Tensile strength	MPa	12.8	15.7	12.3	34.4	30.7
Elongation at break	%	700	120	600	1010	1140
Initial flexural modulus	MPa	150	530	90	30	15
Softening temperature	°C	135	220	132	112	154
Coolant resistances *3						
Volume change	%	1.1	2.4	1.1	2.4	0.1
Tensile strength change	%	-5	-10	4	-61	-41
Elongation change	%	-2	-36	7	-22	-15
Specific gravity	-	0.91	0.83	0.89	1.01	1.05

*1: Content based on 100 % by mass of a total of components. (A1), (A2) and (B).

*2: Content based on 100 % by mass of a total of components (A1) and (A2).

*3: After soaking in distilled water/ethylene glycol = 50/50 (v/v) at 100°C for 168 hours.

Claims

1. A hose, comprising a thermoplastic elastomer having a softening temperature of 160°C or above as measured by a TMA softening temperature measuring apparatus, elongation at break of at least 200% as determined at a testing rate of 100 mm/min, initial flexural modulus of from 20 to 700 MPa as measured at a testing rate of 2 mm/min, and a volume change of -2 to +10% after 168 hours of soaking in a 50%-ethylene glycol aqueous solution at 100°C.
2. The hose according to claim 1, obtained by molding an olefin thermoplastic elastomer comprising:
15 to 95 parts by mass of an olefin resin (A), and
5 to 85 parts by mass of a crosslinked rubber (B), wherein the components (A) and (B) total 100 parts by mass.
3. The hose according to claim 2, comprising the olefin thermoplastic elastomer in which 50 to 97 % by mass of the olefin resin (A) is a 4-methyl-1-pentene polymer (A1),
the polymer (A1) being a 4-methyl-1-pentene homopolymer and/or a 4-methyl-1-pentene/ α -olefin random copolymer containing 80 to 99.9 % by mass of 4-methyl-1-pentene and 0.1 to 20 % by mass of an α -olefin of 2 to 20 carbon atoms.
4. The hose according to claim 3, wherein an olefin resin (A2) other than the 4-methyl-1-pentene polymer (A1) in the olefin resin (A) is a peroxide-decomposable olefin resin.
5. The hose according to any one of claims 2 to 4, wherein the crosslinked rubber (B) is a crosslinked product of a peroxide-crosslinkable olefin copolymer rubber.
6. The hose according to any one of claims 1 to 5, which is an automotive water hose.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP02/03082

A. CLASSIFICATION OF SUBJECT MATTER

Int.Cl⁷ F16L11/04, C08L23/20, C08L21/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

Int.Cl⁷ F16L11/00-11/18, C08L23/00-23/36, C08L9/00-21/02

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	JP 2000-28051 A (Tokai Rubber Industries, Ltd.), 25 January, 2000 (25.01.00), Full description (Family: none)	1-6
Y	JP 11-315965 A (Tokai Rubber Industries, Ltd.), 16 November, 1999 (16.11.99), Full description (Family: none)	1-6
Y	JP 10-287776 A (Asahi Chemical Industry Co., Ltd.), 27 October, 1998 (27.10.98), Full description (Family: none)	1-6

☒ Further documents are listed in the continuation of Box C.
 ☐ See patent family annex.

* Special categories of cited documents: "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier document but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed		"I" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art "&" document member of the same patent family	
Date of the actual completion of the international search 20 June, 2002 (20.06.02)		Date of mailing of the international search report 02 July, 2002 (02.07.02)	
Name and mailing address of the ISA/ Japanese Patent Office		Authorized officer	
Facsimile No.		Telephone No.	

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INTERNATIONAL SEARCH REPORT

International application No.

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C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	JP 9-328588 A (Mitsui Chemicals, Ltd.), 22 December, 1997 (22.12.97), Full description (Family: none)	1-6
A	WO 98/20068 A1 (The Yokohama Rubber Co., Ltd.), 14 May, 1998 (14.05.98), Full description & JP 10-182891 A & JP 10-231963 A & EP 870800 A1 & JP 11-80442 A & US 6166143 A1	1-6

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